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14. ABSTRACT The objective of this workshop is to convene scientists and researchers from top universities in the U.S. and abroad, national laboratories, and the electrochemical industries, and engage in discussion of cutting-edge electrochemical science, in particular addressing issues with respect to the mechanisms of electron transfer. The Center for Electrochemistry (CEC) Annual Workshop on Electrochemistry is a unique symposium that has been held annually at The University of Texas at Austin. This year, a two-day symposium held February 12-14					
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Report Title

Final Report: 2016 CEC Annual Workshop on Electrochemistry

ABSTRACT

The objective of this workshop is to convene scientists and researchers from top universities in the U.S. and abroad, national laboratories, and the electrochemical industries, and engage in discussion of cutting-edge electrochemical science, in particular addressing issues with respect to the mechanisms of electron transfer.

The Center for Electrochemistry (CEC) Annual Workshop on Electrochemistry is a unique symposium that has been held annually at The University of Texas at Austin. This year, a two-day symposium, held February 13-14, 2016, features technical presentations from eleven invited speakers who are experts in fields of engineering, materials, and electrochemistry. They focus on specific electrochemical research topics in three sessions: Advanced Electrolytes with Applications, Lithium-ion Batteries, and Electron Transfer through Films.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

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This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

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Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME

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FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment.

Technology Transfer

2016 CEC Annual Workshop on Electrochemistry

February 13–14, 2016

Each year in Austin, Texas, the CEC Annual Workshop on Electrochemistry brings together experts in fields of engineering, materials, and electrochemistry to focus on a topic in an important area of research. Participants address specific challenges in the field, exchange ideas and information, and catch up with colleagues from around the world. These exclusive workshops feature scientists and researchers from top universities, national laboratories, and electrochemical industries discussing cutting-edge electrochemical science, and addressing issues with respect to the mechanisms of electron transfer. Each workshop features technical presentations and posters from several different perspectives covering areas ranging from electrocatalysis, electrochemical sensors, and electroanalysis.

The Center for Electrochemistry (CEC) at the University of Texas at Austin held its eighth annual electrochemistry workshop February 13–14, 2016 in Welch Hall on the campus of The University of Texas at Austin. There were 147 registered attendees for this conference, including experts from academia, industry, and national laboratories, brought together with the goal of improving understanding in electrochemistry. Three sessions were held sequentially, covering the following topics: advanced electrolytes with applications, lithium-ion batteries, and electron transfer through films. CEC faculty members moderated the sessions and promoted discussion. There was additionally a panel discussion on the topic of DFT and electrochemistry by the speakers from that session.

CEC host Allen J. Bard opened the conference with a discussion of the CEC mission and the request that all participants actively engage the topic. The workshop format allowed for interactive exchange with each of the eleven speakers having a full 50 minutes to present their materials and engage in discussions with the attendees. In addition to these presentations, the meeting featured a poster session and reception. Students and postdocs from UT-Austin and other schools, as well as some industry representatives presented about 40 posters and answered questions from attendees in an informal evening session.

The CEC would like to acknowledge and thank the meeting's sponsors who made it possible: The U.S. Army Research Office (Contract No. W911NF-15-1-0085), The Energy Institute at The University of Texas at Austin, the Cockrell School of Engineering at The University of Texas at Austin, and the Robert A. Welch Foundation (Grant H-F-0037). The views, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

CEC intends to continue a tradition of excellence and host an electrochemistry workshop annually with new topics in important areas of research to be addressed each year. The 2017 meeting will again focus on a variety of current topics in a session format.

AGENDA

Saturday, February 13, 2016

7:30-8:30a Check-in and continental breakfast.

8:30-8:40 Introductory remarks.

Advanced Electrolytes with Applications – C. Buddie Mullins, Moderator

8:45-9:35 **Steven McIntosh**, *Lehigh University*
Structure-function Relationships in Solid Oxide Fuel Cell Electrode Materials
via *In-situ* Neutron Diffraction.

9:40-10:30 **Donald R. Sadoway**, *Massachusetts Institute of Technology*
Molten Salt Electrochemistry: from Energy Storage to Metals Extraction.

10:30-10:50 Break.

10:50-11:40 **Stephen Maldonado**, *University of Michigan*
Electrodeposition of Single Crystalline Semiconductors.

11:40a-1:20p Lunch break.

Lithium-ion Batteries Arumugam “Ram” Manthiram, Moderator

1:20-2:10p **Steven J. Visco**, *PolyPlus Battery Company*
Protected Lithium Metal Electrodes and Next Generation Batteries.

2:15-3:05 **Jason Graetz**, *HRL Laboratories, LLC*
High Energy Conversion Reactions for Lithium ion Batteries.

3:05-3:25 Break.

3:25-4:15 **Bryan D. McCloskey**, *University of California, Berkeley*
An Overview of the Nonaqueous Li-O₂ Battery.

Poster Session, Reception, and Exhibition

4:30-7:00p Posters and reception.

Sunday, February 14, 2016

7:30-8:30a Continental breakfast.

Electron Transfer through Films – Allen J. Bard, Moderator

8:30-9:20 **Henry S. White**, *The University of Utah*
Electron Transfer at the Contact Line of a Gas/Electrolyte/Electrode Interface.

9:25-10:15 **Michael J. Rose**, *The University of Texas at Austin*
Fundamental Aspects of Electron Transfer through Ultrathin Film Metal
Oxides (Al₂O₃, TiO₂) on Semiconductors

10:15-10:35 Break.

10:35-11:25 **Justin Gooding**, *The University of New South Wales*
Switching On and Off Electrochemistry at Monolayer Modified Si Electrodes
using Light: from Electrode Arrays to Single Cell Capture and Release.

11:30a-1:10p Lunch break.

1:10-2:00p **David J. Fermín**, *University of Bristol*
Charge Transfer across Thin Organic Films at Semiconductor Surfaces.

2:05-2:55 **Shigeru Amemiya**, *University of Pittsburgh*
Nanoscale Scanning Electrochemical Microscopy of Graphene and Graphite.

2:55-3:15 closing remarks.



2016 CEC Workshop speakers (from left): Steve Visco, Bob Villwock, Henry White, Bryan McCloskey, Donald Sadoway, Shigeru Amemiya, Justin Gooding, Steven McIntosh, David Fermín, Stephen Maldonado, Jason Graetz. Not pictured: Michael Rose.

I. Advanced Electrolytes with Applications Session

Steven McIntosh, *Lehigh University*

“Structure-function Relationships in Solid Oxide Fuel Cell Electrode Materials *via In-situ* Neutron Diffraction.”

Dr. McIntosh’s presented research on electrode materials for solid oxide fuel cells (SOFC). SOFCs are useful in intermediate scale electric power supply applications such as office buildings. They run at temperatures in excess of 750°C and typically run oxygen reduction at the cathode and methane oxidation at the anode. The electrode materials of interest are mixed ionic-electronic conductive (MIEC) perovskite oxides of the general form $ABO_{3-\delta}$. In these materials, oxygen anion transport occurs by vacancy hopping, and the oxygen content depends upon temperature and the partial pressure of O_2 .

Oxygen stoichiometry, $3-\delta$, is a critical parameter in determining both ionic transport and likely surface exchange. There is a lot of scatter in the literature for these data.

Dr. McIntosh explained how *in-situ* neutron diffraction is a powerful tool to characterize materials under fuel cell conditions. All of the relevant mixed ionic-electron conducting (MIEC) properties must be carefully, separately measured: *in-situ* neutron diffraction for structure, oxygen stoichiometry, and anion displacement; pulsed isotope exchange on powder for surface rate (a direct measurement of oxygen exchange as a chemical reaction rate); and XPS and high-sensitivity, low-energy-ion scattering (HS-LEIS) for surface composition, where HS-LEIS can provide the outermost surface composition. These measurements combine to predict electrode performance and serve to test the hypothesis that there is some link between bulk and surface properties of MIECs.

One possible conclusion is that the true outer surface kinetics does not limit performance. More work is required. The bulk transport parameters correlate with the surface exchange rate. The surface composition does not correlate with the surface exchange rates.

There was some discussion at the conclusion of the talk on the questions of what do we mean by “surface”? Do the surface kinetics ever limit performance? Where can we use the measured k values and where should we use caution? Is it sufficient for an electrode model? For fundamental insights?

Donald Sadoway, *Massachusetts Institute of Technology*

“Molten Salt Electrochemistry: from Energy Storage to Metals Extraction”

Perhaps one of the greatest barriers to widespread use of renewable energy today is the storage of electrical energy. Without any storage capacity, electricity demand must be in constant balance with electricity supply. If there is a problem with delivering electricity from wind power, coal burning, etc., there must be back-up generators that will compensate for the electricity loss at a given point in time. As such, many different technologies are being developed for grid-level energy storage, such as lithium-ion batteries, redox flow batteries, and liquid metal batteries, with the hope to store electrical energy in chemical bonds until a population needs that electricity. Dr. Sadoway discussed the liquid metal battery as a potential solution to grid-scale energy storage.

The liquid metal battery may have many potential applications, as it has a large energy density and utilizes relatively inexpensive and earth-abundant materials (magnesium and antimony). The battery works by melting metals and operates based on the different densities of the metals. For instance, magnesium is a lighter metal than antimony. During the discharging process, when electrons are being used for society’s purposes, magnesium gives up two electrons, migrates across the salt barrier, and accepts two electrons from antimony. This magnesium-antimony alloy is stable in the discharge state. The opposite reaction occurs when the battery is being charged, and a battery can be charged on the grid from solar power, wind power, and other green technologies. Because of this, Sadoway believes that his battery will revolutionize the field of electrochemical energy storage.

Stephen Maldonado, *University of Michigan*
“Electrodeposition of Single Crystalline Semiconductors”

Professor Maldonado presented his group’s pioneering research on electrochemical liquid-liquid-solid (Ec-LLS) deposition, a new electrochemical deposition method for low temperature growth of crystalline materials. The major barrier to achieving desired crystallinity by traditional electrochemical deposition methods is that the growth kinetics favor an amorphous structure at low temperatures. Dr. Maldonado’s strategy takes advantage of the unique properties of liquid metals such as Hg and Ga to serve both as electrode and solvent for crystalline growth. The deposition mechanism begins when molecular precursors in solution are reduced to zerovalent species at the liquid metal/solution interface. The reduced species then partition into the liquid metal and diffuse to the solid/liquid metal interface where they precipitate as a monocrystalline material. The diffusion rates of the reduced species are the rate-limiting step in the overall growth kinetics, which can be precisely tuned simply by optimizing the applied potential/current.

The Maldonado group has synthesized a range of crystalline group IV and III-V semiconductors by the Ec-LLS method at or near room temperature in simple solvents like water and propylene carbonate from inexpensive precursors of low toxicity. The major practical advantages of the Ec-LLS strategy over more traditional chemical vapor deposition of crystalline semiconductors include the much lower cost of instrumentation and power input, more precise control over growth kinetics, and compatibility for growing thermally sensitive materials. The deposition technique was also modified to produce uniformly micro- and nanostructured arrays of the semiconducting materials by appropriate templating of the liquid metal. Dr. Maldonado ended the presentation with a major recent highlight, the conformal Ec-LLS deposition of single-crystal Ge over an entire square inch of area at room temperature, demonstrating the potential of the deposition method to drastically reduce costs associated with the preparation of crystalline semiconductors for photovoltaic applications.

II. Lithium-ion Batteries

Steven J. Visco, *PolyPlus Battery Company*
“Protected Lithium Metal Electrodes and Next Generation Batteries”

Lithium metal is an ideal anode material for any lithium-based secondary battery system because of its low negative electrochemical potential (-3.040 V vs SHE) and high gravimetric capacity (3860 mAh/g). However, non-uniform lithium deposition and stripping during charging and discharging leads to uncontrollable dendrite growth and poor coulombic efficiency. This has limited the practical application of these electrodes. Achieving reversible, efficient and safe operation of lithium metal anodes can enable the realization of many next-generation high energy density systems, including lithium-air and lithium-sulfur. In addition, a water-stable protection layer on the lithium metal surface would enable the use of aqueous electrolytes in these systems, and thus improve safety and cyclability.

PolyPlus has developed a protected lithium metal anode by coating a layer of solid electrolyte with high lithium-ion conductivity on the surface of the lithium metal. A liquid, gel or solid interlayer is introduced between the metal surface and solid electrolyte to enable a conformal

interfacial contact between them, and to prevent any reaction between the two layers. The solid electrolyte layer typically has a LISICON structure, such as LATP, $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$. This is water stable, and hence allows its use in an aqueous environment. The use of a solid-electrolyte layer also enables an extended voltage range of operation in aqueous systems beyond the electrochemical stability window of water. The whole protected electrode is sealed in a flexible compliant seal that accommodates the volume changes in the lithium metal layer.

The application of these protected lithium metal electrodes was demonstrated in a primary aqueous lithium air cell, which uses a gas diffusion cathode that utilizes ambient oxygen in the atmosphere. Energy densities of 800 Wh/kg were achieved in such systems. They were also used in the so-called lithium-water systems that utilize dissolved oxygen in seawater as the cathode, and demonstrated energy densities of 1300 Wh/kg. The protected lithium metal electrodes were also used in secondary aqueous lithium air cells that used a multiprotic organic acid, such as malonic acid, in the electrolyte to prevent side reactions with ambient CO_2 . It was found that the LATP solid electrolyte layer remained stable even at very low pH. The cells were found to cycle stably and reversibly for up to 75 cycles with a nearly 80% Coulombic efficiency.

PolyPlus has demonstrated the application of these protected lithium metal electrodes in aqueous lithium sulfur batteries. One advantage of aqueous lithium sulfur batteries is the high solubility of the discharge product Li_2S in water. To take advantage of the fact that nearly 80% of the capacity of a lithium sulfur battery between the polysulfide intermediate Li_2S_4 and Li_2S , an aqueous catholyte of dissolved polysulfides was used with a carbon fiber cloth as the cathode. No hydrogen evolution was found during discharge at voltages up to 1.65 V. The cell have been cycled for more than 100 times between cutoff voltages of 2.8 to 2 V. These aqueous lithium sulfur batteries are projected to have an energy density of up to 500 Wh/kg.

Jason Graetz, HRL Laboratories

High Energy Conversion Reactions for Lithium-ion Batteries

Conventional, commercialized lithium-ion batteries use intercalation chemistry, in which the lithium ions are inserted and stored in the interplanar spaces of layered materials such as graphite and LiCoO_2 . These materials have been successful because the lithium insertion chemistry is fast and reversible, but their capacities are limited by the total available sites for lithium storage and the “one-electron-barrier” problem where only one electron is usable per metal atom, regardless of how many oxidation states it may possess. In the future, new chemistries will be needed to circumvent this problem and achieve higher capacities.

A potential new chemistry in lithium-ion rechargeable batteries is the *conversion* chemistry, which has until now typically only been used in non-rechargeable batteries. With this chemistry, the entire material participates in the reaction and all oxidation states are used, leading to much higher capacities. Of particular interest to Graetz was the material FeF_3 , which potentially has a capacity nearly four times higher than LiCoO_2 . He found that during lithiation, the lithium first inserts into the FeF_3 matrix to form LiFeF_3 , followed by a conversion step to form FeF_2 and LiF . Following this, he found a second conversion reaction occurred, ultimately forming Fe and more LiF . Using transmission electron microscopy and electron diffraction techniques, Graetz determined that the particles underwent no noticeable morphological changes when these reactions occurred, but that the particles expanded to accommodate the lithium. He also determined that the particles were comprised of a bicontinuous, interpenetrating network of Fe

nanodomains embedded within an amorphous LiF matrix. The interconnectedness of the Fe nanodomains formed a conductive network that allowed this reaction to proceed reversibly.

Graetz noted two downsides to this material. The first was the small particle size needed since bulk lithiation in conversion-based materials is much slower than in intercalation-based materials. The second was that there was a large hysteresis separating the charge and discharge voltage curves, meaning large energy losses in a real battery. He put forward two potential causes for this hysteresis: 1) that it may not be related to kinetics and may instead be intrinsic as a result of asymmetric reaction pathways, or 2) that there may be a compositional inhomogeneity within the particles between the end of charge and the start of discharge.

Additionally, Graetz tested another conversion material, CuF_2 , and found that the reaction pathway was similar but irreversible. To rectify this irreversibility, he added Cu to the FeF_3 he tried previously and found that the reaction became reversible and exhibited very low hysteresis.

Bryan D. McCloskey, *University of California, Berkeley*
An Overview of the Nonaqueous Li-O₂ Battery

The lithium-ion (Li-ion) battery has been the state-of-the-art portable rechargeable battery for the past few decades, and has reached an energy density of roughly 120 Wh/kg. Several high-energy battery alternatives (*e.g.*, Li-air, Li-S, *etc.*) have been proposed to reach the new energy density target of 400 Wh/kg in 2017, which has been set by the Joint Center for Energy Storage Research (JCESR). However, none of these battery systems is yet a commercial reality due to challenges in rechargeability and safety. The lithium-oxygen (Li-O₂) battery, which has the maximum theoretical energy density, is the research focus of McCloskey's group. To develop an advanced battery with high energy density and low cost, a program has been designed by his group to answer the fundamental electrochemistry questions such as what is eliminating the battery from achieving high energy density, reversibility and long lifetime.

The critical issues are: 1) The energy capacity of the system is only a small portion of the theoretical capacity dictated by the amount of Li in the system; 2) The charge overpotential is higher than the discharge overpotential. These issues need to be understood from a chemistry point of view to improve the battery's energy efficiency and rechargeability. McCloskey's group designed a battery system that can quantify the amount of O₂ consumed and evolved by monitoring the gas pressure change and analyzing the gas content. Li₂O₂ was found to be formed on the surface of the electrode, and it can be quantitatively determined using iodometric titration. By comparing the amount of e^-/O_2 during discharge and the amount of $\text{e}^-/\text{Li}_2\text{O}_2$ during charge in a variety of solvent systems, it is found that there is always slightly less Li₂O₂ formed than O₂ consumed, which is nonideal for a battery system. This difference could be ascribed to parasitic reactions involving Li₂O₂ and electrolyte decomposition. McCloskey's group has further probed this phenomenon by building a cell using a carbon electrode containing ¹³C. After Li₂O₂ is formed on the electrode, an oxidation reaction occurs and forms Li₂¹³CO₃, because Li₂O₂ is a strong oxidizer. Both O₂ and ¹³CO₂ were found to evolve in the charge process. The amount of the O₂ evolution during charge is less than the O₂ consumed during the discharge. Thus, and it is preferable to eliminate CO₂ to make the battery more reversible.

McCloskey pointed out a misconception that high overpotentials can be improved by using catalysis without first understanding the chemistry that induces the overpotential. McCloskey demonstrated that Li_2O_2 is insoluble in nonaqueous electrolyte and can deposit on the interface of the electrolyte and the electrode. As the cycle number goes up, the formation of C- Li_2O_2 on the surface of the electrode blocks oxygen evolution and leads to a passivation effect. Thus Li_2CO_3 drives the overpotential in the charge process. Until a certain potential is reached, an enormous amount of CO_2 is evolved during the process. This is the critical issue in the Li- O_2 battery and the development of new electrolytes and the cathodes that are stable is important.

McCloskey's group also examined how the formation of Li_2O_2 in the cell affects the battery's performance. A reduction of the cell potential has been observed as the current increases, which leads to reduced energy capacity. This is due to electronic insulation of insoluble Li_2O_2 deposited on the electrode. As a result, a huge charge transfer resistance is formed on the electrode surface. If one can eliminate Li_2O_2 from coating the surface of the electrode, then the capacity of the system can be increased. McCloskey showed that the electrolyte plays a very important role in controlling the deposition of Li_2O_2 . A highly Lewis basic electrolyte or incorporation of water in the system can both increase the solubility of Li_2O_2 and improve stability. An XRD image showed a toroid-like surface feature growing as the deposition of Li_2O_2 decreased. The counter-ion to lithium in the system can also influence the system's stability. For example, LiNO_3 can also introduce the toroid-like structure. Entirely removing the organic electrolyte in the system and only having LiNO_3 as the electrolyte is shown to improve the electrolyte's stability and generate very low overpotential for long cycles.

III. Electron Transfer through Films

Henry S. White, *The University of Utah*

Electron Transfer at the Contact Line of a Gas/Electrolyte/Electrode Interface

The fundamental study of nanoscale bubbles at solid/water interfaces is of significant interest because of the prevalence of the phenomenon in many important processes. By investigating the nucleation, formation and stability of a single nanobubble, researchers will be able to extend understanding of mass transport theory to the nanoscale. However, isolating a single nanobubble and studying it is very difficult. White's group has established a well-confined system to generate H_2 nanobubbles electrochemically at a nanosized Pt electrode surface and then study the properties of the nanobubble *in situ*.

Pt nanoelectrodes with 10–100 nm diameter were fabricated by etching Pt wire sealed by glass. Due to the hydrophobicity of glass and hydrophilicity of “dirty” Pt, when the hydrogen evolution reaction (HER) is run at the electrode, H_2 gas is pinned at the electrode surface and forms a nanosized bubble. White's group confirmed the formation of this nanobubble by running CV at the Pt electrode in acid solution. They observed a sudden decrease to almost zero current (remaining current) soon after HER happened, which can be attributed to the coverage of the H_2 bubble blocked the electron transfer from bulk solution to the electrode surface.

According to Henry's law and Laplace-Young equation, the internal pressure and surface tension should be very high if the bubble has a diameter at nano scale and the solubility of gas into

solution will be much higher than ambient condition. White's group explained the stability of the formed nanobubble as the electron transfer at the contact line of a gas/electrolyte/electrode interface. Constant influx of newly formed H_2 at the edge of Pt electrode compensates the diffusion of the bubble out to the bulk solution, which helps to maintain a stable bubble. White's group used COMSOL to simulate the width of this contact line to be 0.06 nm. In comparison, the size of one Pt atom is 0.3 nm. This result suggests that only sub-atom size contact line at the electrode edge will be enough to support the nanobubble. White's group further studied the nucleation process and life time of the nanobubble by changing acid solution and scan rate, they found that a supersaturation of 300-fold is necessary for the nucleation, the smallest nucleate size is 3.4 nm and the life time of a bubble is at nanoseconds level. White's group also studied N_2 and O_2 nanobubbles and found similar results.

Michael J. Rose, *The University of Texas at Austin*

“Fundamental Aspects of Electron Transfer through Ultrathin Film Metal Oxides (Al_2O_3 , TiO_2) on Semiconductors”

Professor Rose's talk was directed at fundamentals of a scheme for preventing corrosion at semiconductor-liquid interfaces by atomic-layer deposition (ALD) of thin oxide layers. Some key questions he is investigating include how thin must these layers be in order to protect the electrode but still allow electron transfer, and what can be done to improve electron transfer through these layers.

The presentation had four main topics: (1) The effect of Pt nanoparticles on kinetics of electron transfer (ET) through Al_2O_3 from an underlying semiconductor electrode, (2) Simulation of band diagrams and this ET behavior, (3) Interfacial effects on ET through $Si| -R |TiO_2$ constructs, and (4) Applications of R-modification of $Si(111)$ for the hydrogen evolution reaction (HER).

Justin Gooding, *University of New South Wales*

Switching Electrochemistry On and Off at Monolayer Modified Silicon Electrodes Using Light

Electrode arrays have many applications, especially in the biological and medical fields, but are limited by three core issues. First, there is limited space on the chip, and sometimes hundreds of wires are needed. Secondly, complicated electronics on the chips not only limit the size of the chip, but limit the functionality as well. Finally, the predefined required in standard chips limit the capability of such devices. In response to these problems, Gooding's group has prepared devices using the semiconducting properties of silicon. These devices only have one lead, and under depletion, light can be used to photo-excite a certain region of the wafer and thereby localize the electrochemical reactions used for analysis, significantly simplifying the typical array design.

To prepare these devices, $Si(100)$ was used as, presently, it is the industry standard. After the native oxide was removed via HF, the hydrogen-terminated surface was prepared with ammonium fluoride. The silicon was then hydrosilylated using the method developed by Chidsey

with a long functionalized alkyl chain. Using click chemistry, these surfaces are then functionalized for various applications explored throughout the talk. At first, diffusion posed a problem and severely reduced resolution, but resolution has been improved 300 μm for a 500 μm thick strip. Resolution was improved by varying several properties, including notably, the intensity of the light. More intense light limited the localization of the reaction as more carriers were generated. Further, by adjusting the potential to which the silicon was held, resolution could be refined.

In order make the photoelectrochemical arrays bio-sensitive, surfaces were functionalized with a certain strand of DNA, and the array was used to test for the strand's compliment. Using the strands of DNA natural affinity for each other and the effect of complimentary binding on charge transfer, the presence of the molecule could be detected and localized. Gooding showed images of tests using the perfect and partial compliments, and sequences containing no compliments, and it is clear that the arrays are capable of localizing and detecting the sequence. In another study, antibodies were attached to the end of the molecule and used to image cells.

David J. Fermín, *University of Bristol*

Charge Transfer across Thin Organic Films at Semiconductor Surfaces

Understanding charge transfer across semiconductor-insulator-metal electrode surfaces is critical to designing new nanostructure devices for applications such as solar energy conversion and storage. In order to systematically design any nanostructure device, electron transfer can be locally electrochemically evaluated at each interface and consequently tuned with respect to the sum of its parts in the device. For instance, one approach for evaluating nanostructure electrodes utilizes electrochemistry to map the density of states (DOS) of the metal electrode to the Fermi level of the redox species ($E_{\text{F}(\text{redox})}$). Under equilibrium conditions, the concentration of reactants (the redox species) remains the same and the resulting Nernst potential assumes fast, isoenergetic electron transfer where $E_{\text{F}(\text{redox species})} = E_{\text{F}(\text{metal electrode})}$. One possible deviation from equilibrium conditions would be a change in the concentration of redox species in solution. Changing the concentration of redox species results in an overall change in entropy for a given system. This is due to an altered electron delocalization sphere (or new outer-sphere reorganization solvation energy) for electron transfer at the metal electrode, which will consequently result in a different rate of electron transfer.

Fermín has utilized these critical fundamental facets of electrochemistry in order to probe nanoparticle mediated electron transfer in various nanoarchitecture systems. For instance, Fermín has studied quantum dot model systems of CdTe and CdSe of various sizes and their charge transfer dynamics with electrode surfaces. By studying quantum dots of different sizes and compositions, Fermín found that increasing DOS near the Fermi redox energy has a pronounced effect on electron transfer kinetics of nanoparticle-insulator-electrode architectures. Due to luminescent properties, the rate-determining step of electron transfer is modulated by charge injection to individual quantum dots. A quantum dot's optical band gap is dependent on the particle size, so Mott-Schottky analysis of the band energies of the quantum dots were used. This showed that, as the particle size increases, the valence band edge of the CdTe particles approaches the redox energy of the redox couple in solution ($\text{Fe}(\text{CN})_6^{3-/4-}$), while

the band edge energy of the $(\text{Fe}(\text{CN})_6)^{3-/4-}$ remains above the band edges of the CdSe particles. Consequently, the size-dependent enhancement of quantum-dot-mediated charge transfer was linked to the overlap between the DOS corresponding to the reduced species in solution and the resultant DOS of the quantum dots valence band near the valence band edge. From this study, Fermín was able to find that the tunneling rate constant is independent of CdTe dot size, therefore the main indicator for determining the charge transfer mediation is the mismatch between the redox solution species $(\text{Fe}(\text{CN})_6)^{3-/4-}$ band edge and the valence band edge.

Fermín has found that charge transfer dynamics in these quantum-dot-insulator-electrode systems are dominated by the density of states (DOS) at the Fermi redox level. In particular, when the overlap of the energy levels of the nanoparticle and redox species is strong, electron transfer can be efficient, even across insulating monolayers.

Shigiru Amemiya, *University of Pittsburgh*

Nanoscale Scanning Electrochemical Microscopy of Graphene and Graphite

Pushing electrochemistry to the nanoscale is a tall order, as it incorporates many different chemical and engineering issues. On the chemical side, the cleanliness of the electrolyte and analyte of interest is very important. On the engineering side, fabricating electrochemical probes that are on the order of tens of nanometers requires trial and error, keeping in mind the various impurities associated with fabricating such electrodes as well as how electrostatic discharge can effect the electrode surface.

Dr. Amemiya's talk focused on this push to smaller levels in electrochemistry. He presented a brief overview of some of the challenges he and his group have faced in moving to this level. Amemiya discussed the cleanliness of the electrode and the effect non-specifically adsorbed species on an electrode surface can have in studying heterogeneous rate kinetics at tiny electrodes. One particular experiment looked at the cleanliness of highly oriented pyrolytic graphite (HOPG). Amemiya's group found that this surface becomes riddled with impurities over time, whether it is sitting in solution or sitting in air. Evidently, the largely hydrophobic surface structures will allow hydrophobic adsorbers to sit on the electrode. Through various experiments, Amemiya showed that these challenges could be overcome if one takes extensive care of the electrode surface. Through these exhausting efforts, Amemiya's group was able to measure the very fast heterogeneous electron transfer kinetics of the reduction of ruthenium hexamine, which gave them the largest rate constant ever recorded in electrochemical experiments.

Poster Session

Caleb Alexander & Will Hardin	<i>Synthesis of Perovskites and Support Interactions towards the Catalysis of the Oxygen Evolution and Reduction Reaction</i>
Pedro de Souza	<i>Investigation of Li Dendrite Growth with TOF-SIMS</i>
Paul DeGregory	<i>Quantitative Electrochemical Metalloimmunoassay for TFF3 in Urine using a Paper Analytical Device</i>
Jeffrey Dick	<i>Studying Nascent Electrocatalysts on Ultramicroelectrodes Atom by Atom</i>
Jeffrey Dick	<i>Electrochemically Identifying and Differentiating Cancerous Cells from Healthy Cells</i>
Ming Fang	<i>Molecular Behavior on Heterogeneous Metal Surfaces Revealed by Sum Frequency Generation Microscopy</i>
Pablo Fanjul-Bolado	<i>Non-enzymatic Ethanol Sensor Based on a Nanostructured Disposable SPE</i>
Pablo Fanjul-Bolado	<i>Electrochemical Immunoassay Based on a 96-well Screen-printed ELISA Plate</i>
Pablo Fanjul-Bolado	<i>Hydroquinone Diphosphate/Ag⁺ as an Enzymatic Substrate for Alkaline Phosphatase Catalyzed Silver Deposition</i>
Robin Forslund	<i>Nanostructured LaNiO₃ Perovskite Electrocatalyst for Enhanced Urea Oxidation</i>
Jerzy Gazda	<i>Advances in Energy Storage: Lithium-ion Battery Performance using MOLECULAR REBAR®</i>
Guillaume Goubert	<i>Probing Electrochemistry at the Nanoscale with Tip- and Surface-enhanced Raman Spectroscopy</i>
Wenlong Guo	<i>CuV₂O₆ and Cu₂V₂O₇: Two Photoanode Candidates for Photoelectrochemical Water Oxidation</i>
Mohammad Abul Hasnat	<i>Influence of Electrode Assembly on Catalytic Activation and Deactivation of Pt Film Immobilized H⁺ Conducting Solid Electrolyte in Electrocatalytic Reduction</i>
Caleb Hill	<i>Optical Correlation of NP-UME Collisions via Light Scattering</i>
Liang Hong	<i>3D Phase-field Modeling of Domain Structure Formation Kinetics in Partially (de)lithiated LiFePO₄ Particles</i>
Seyyedamir Hosseini	<i>Electrochemical Detection of Heavy Elements Using Thiol-capped Gold Nanoparticles</i>
Hsien-Yi (Sam) Hsu	<i>A Liquid Junction Photoelectrochemical Solar Cell Based on p-Type MeNH₃PbI₃ Perovskite with 1.05 V Open-circuit Photovoltage</i>
Kara Kearney	<i>Simulation of Charge Transport Mechanisms Across Solid/Electrolyte Interfaces</i>
Dipankar Koley	<i>Realtime Microbial Metabolic Exchange: as Studied by Scanning Electrochemical Microscopy (SECM)</i>
Dillon Kopecky	<i>Gold Single Crystal Electrodes as a Support for Cobalt Monolayers to Study the Electrochemical Evolution of Oxygen</i>

Karl Kreder	<i>Aliovalent Substitution of V^{3+} for Co^{2+} in $LiCoPO_4$ by a Low-temperature Microwave-assisted Solvothermal Process</i>
Xiang Li	<i>Low Voltage Paper Isotachophoresis Device for DNA Focusing</i>
Long Luo	<i>Theoretical and Experimental Approach for Correlating Nanoparticle Structure and Catalytic Activity</i>
Niyi Mabayoje	<i>The Role of Anions in Metal Chalcogenide Oxygen Evolution Catalysis: Electrodeposited Thin Films of Nickel Sulfide as “Pre-catalysts”</i>
Rafael Masitas	<i>Electrochemical Deposition of Intact Gold Nanoparticles onto Electrode Surfaces</i>
Jeremy Meyers	<i>Performance Improvements in Industrially Produced Lead-acid Batteries with MOLECULAR REBAR®</i>
Melissa Meyerson	<i>Study of Dendrite Growth for Improved Lithium-ion Batteries</i>
Craig A. Milroy	<i>Bio-pseudocapacitance: An Electroactive Hydrogel Synthesized from Endogenous Biomolecules</i>
Cesar Ortiz	<i>Detection of Single Metal Nanoparticles using Electrocatalytic Amplification and Atomic Force Microscopy</i>
Nevena Ostojic	<i>Electrocatalytic Reduction of Oxygen on Platinum Nanoparticles Confined to Ultra-thin, Insulating Oxide Films</i>
Ryan Pekarek	<i>Composite $n\text{-Si}(111) R$ Metal-oxide Photoelectrodes: Effect of Interfacial Organic Linkers on Charge Transfer and ALD Growth</i>
Waynie Schuette	<i>Electroactive and Conductive Polymers for Aerospace Applications</i>
Iqbal Ahmed Siddiquey	<i>Electrocatalysis of Coinage Metal Nano Particles</i>
Lauren Strawsine	<i>Enzymatically Enhanced Collisions on Ultramicroelectrodes for the Detection of Femtomolar Levels of Cytomegalovirus in Urine</i>
Ding Tang	<i>Facile Growth of Porous $Fe_2V_4O_{13}$ Films for Photoelectrochemical Water Oxidation</i>
Sean Wood	<i>Simple Additive Could Enable the Use of Lithium Metal Anodes and Increase Battery Capacity by 10x</i>
Bryan Wygant	<i>Structural and Catalytic Effects of Iron- and Scandium-doping on a Strontium Cobalt Oxide Electrocatalyst for Water Oxidation</i>
Ji Zhao	<i>Impurity Control of a Silicon Film Electrodeposited in Molten Salt: One Step Towards Solar Cell</i>